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(54) Property determination

(57) A method of determining or predicting a value P_x of a property (e.g. octane number) of a material X or a property of a product of a process from said material or yield of said process, which method comprises measuring the absorption D_{ix} of said material at more than one wavelength in the region 600-2600 nm, comparing the said absorptions or a derivative thereof with absorptions D_{im} or derivatives thereof at the same wavelength for a number of standards S in a bank for which the said property or yield P is known, and choosing from the bank at least one standard S_m with property P_m said standard having the smallest average value of the absolute difference at each wavelength i between the absorption D_{ix} (or derivative thereof) for the material and the absorption D_{im} (or derivative thereof) for the standard S_m to obtain P_x , with averaging of said properties or yields P_m when more than one standard S_m is chosen.

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Description

This invention relates to a method of determining or predicting by near infra red (NIR) spectroscopy properties of feeds or products and/or yields in physical or chemical processes or separations, in particular involving hydrocarbons, especially in hydrocarbon refineries

NIR spectroscopy has many advantages over other methods of analysis in refineries and can cover a large number of repetitive applications accurately, quickly and on line. The NIR region between 800 and 2500nm contains the totality of molecular information in the form of combinations and overtones from polyatomic vibrations, but Mathematical techniques are needed to exploit this information and to calculate the desired parameters. EP-A-285251, 304232, 305090, the disclosure of which is hereby incorporated by reference, describe the use of NIR for determining octane number, yields and/or properties of a product of a chemical process or separation process from analysis on the feeds to that process, and yields and/or properties of a product of a blending operation again from analysis on the feed thereto.

At present, numerical methods described for modelling physicochemical properties based on NIR spectra all are of a correlative nature and involve relations of a regressional character between the property(ies) studied. Among these multivariable analyses are multilinear regression (MLR), Principle Component Regression (PLR), Canonic regression, and regression by Partial Least Squares (PLS). In all cases there is sought between the property and the NIR spectrum a relation which may be linear but is usually quadratic or of higher algebraic form involving regression coefficients applied to each absorption. The establishment of any regression requires a progressive calibration, as the approach is empirical and not supported by a theory

These techniques have disadvantages, the chief of which is the need for establishing a strong correlation between the spectrum and the property, and their difficulty in dealing with positive or negative synergy between components contributing to that property. For example for determining chemical composition e.g. LINA (linear, isoparaffin, Naphthenic, Aromatics) in a hydrocarbon feed to a catalyst reformer, a PLS technique based on the NIR spectra has been described for use. The model works well on the calibration set but the response of the models when pure hydrocarbons are added e.g. cyclohexane is not satisfactory, as the model predicts changes in isoparaffins and naphthenes the reverse of that found experimentally. Furthermore there are other practical difficulties, mainly in the need to identify samples of families having the same kind of relation between the spectra and the properties to be modelled. Thus the model may be limited especially with a non linear relation between spectrum and property. Especially when at the edges of the available data the accuracy of the model diminishes. The stability of the model is also a problem, as is the need when adding new standards to do laborious revisions to give the new model, especially when adjusting to a new feedstock for a process; thus testing 6 properties on 4 products leaving a distillation unit requires 24 models, each of which has to be changed for each change of the feed not included in the calibration.

We have discovered a new approach avoiding the above problems with correlations, and regression calculations, and being capable of being expanded automatically with use of a new product of different quality.

The present invention provides a method of determining or predicting a value P_x of a property of a material X or a property of a product of a process from said material or yield of said process, which method comprises measuring the absorption D_x of said material at more than one wavelength in the region 600-2600nm, comparing the said absorptions or a derivative thereof with absorptions D_m or derivatives thereof at the same wavelengths for a number of standards S in a bank for which the said property or yield P is known, and choosing from the bank at least one and preferably at least 2 standard S_m with property P_m , said standard S_m having the smallest average values of the absolute values of the difference at each wavelength λ between the absorption D_x (or derivative thereof) for the material and the absorption D_m (or derivative thereof) for the standard S_m to obtain value P_x , and with averaging of said properties or yields P_m , when more than 1 standard S_m is chosen.

The above method can be performed without regression or correlation techniques.

Thus for the performance of the method of the invention, a bank is prepared in which the NIR spectra are recorded at many wavelengths for a large number of standard materials, together with their properties (or those of products obtained by processes therefrom) determined by alternative techniques e.g. gaschromatography for chemical compositions and yields determined by known methods. The standards are chosen to cover the area in which the method is to be used, so for octane number determination, a range of gasolines is chosen of widely varying octane numbers, with different contents of lead, or other additives such as alkyl ethers and aromatics. The number of wavelengths chosen may be 2-1000 e.g. 5-200 or 10-20 such as 40-80 while the number of standards can be at least 100 or 1000, or 100,000 up to 5 million depending on property(ies) chosen.

The wavelengths chosen may be at regular intervals such as each 1-50 or 15-35nm (or each 1-5nm or each nanometre) or may be at irregular intervals e.g. with intervals of 1-200nm e.g. 1-100 or 1-50 such as 4-50 or 10-60nm, which may be (random or chosen because of a change in the shape of the spectral curve at that wavelength e.g. a peak, trough or shoulder. The wavelengths may be in the region 600-2600nm, such as 800-2600nm, in particular 1500-2600 or 2000-2550nm, or 800-2000 especially 1000-1800nm for diene containing gasolines such as ones produced by cracking e.g. steam cracking. The wavenumbers may be in the region 16,600-3840 cm^{-1} , e.g. 12,500 to 3840 cm^{-1} in particular 6660-

3840 or 5000-3900cm⁻¹, or 12500-5000 especially 10000-5500cm⁻¹; corresponding frequencies in Hertz can be obtained by multiplying this wavelength by 3x10¹⁰cm/sec.

The absorptions for the unknown sample are compared with the absorptions at the same wavelength of the standards, and those standards chosen having the smallest differences. The properties of those chosen standards are then averaged to determine the property of the unknown sample. The absorptions at more than one wavelength may be chosen, e.g. 2-1000 such as 5-100 or 10-20.

In the method of the invention the standards chosen are those with the smallest average values of the absolute difference at each wavelength i between the absorption/optical density (or a derivative thereof) D_{ix} for the unknown material and the corresponding absorption/optical density (or derivative thereof) D_{im} for the standard. The averages may be in respect of the mean value of $D_{ix}-D_{im}$ (whatever its sign i.e. absolute difference), or $(D_{ix}-D_{im})^2$ and may be the simple mean value or the differences may be weighted to take account of the different sensitivity of the absorption to the property at that wavelength or the different sensitivity of the spectrometer at that wavelength. For each standard in the bank of standards for the type of material in question, the average difference is found as described and the standard or standards with the smallest average differences chosen, e.g. at least 1 but preferably at least 2 such as upto 1000 smallest such as 1 (or 2)-100 or 1 (or 2)-20 but is particular 1 (or 2)-10 and especially 2-6 smallest. Advantageously the average differences chosen and hence the standard (or standards) S_m chosen for the property or yield wanted are such that in relation to the unknown material X and each chosen standard S_m the following functions is met

$$\frac{i_{xm}}{\sum D_{ix}} < \text{experimental error}$$

wherein i_{xm} is the proximity index and is defined by $i^2(xm) = \sum (D_{ix} - D_{im})^2$ and the experimental error is in determining said property or yield in the standard. The value P_x of the property or yield is the same as property or yield P_m or the average P_m if more than one standard S_m is chosen.

In order to aid the choice of the appropriate standards, especially in relation to a large number of wavelengths for a complex unknown mixture, it is preferred to limit the choice to those defined by means of a minimal index. For the chosen 'standard' the minimal index is at least the same as the differences between the absorptions of the unknown and the standards. Mathematically, this may be expressed as $i^2_{ab} = i^2_M$ where iM is the minimal index for the property, and iab is a measure of the deviation (called the proximity index) at all the chosen wavelengths between absorption of the unknown and a chosen standard b . That measure is defined by

$$i(ab)^2 = \sum_i (D_{ia} - D_{ib})^2 \quad (1)$$

where D_{ia} is the optical density (or absorbance) of unknown a at wavelength i (or a derivative thereof e.g. a first, second or third derivative of that density), and D_{ib} is the optical density (or absorbance) of standard b at that wavelength i (or a derivative thereof e.g. a first, second or third derivative of that density). The value of D_i is the optical density or the optical density difference with respect to the baseline of the spectrum at that wavelength, or the baseline interpolated between 2 wavelengths on either side thereof.

If desired instead of the optical density D_i a normalized density W_i may be used where $W_i = D_i / \sum D_i$. This normalization avoids errors due to small electronic fluctuations in the apparatus and compensates for small differences in the optical path between the optical cells. In this case the proximity index is defined by

$$i(ab)^2 = \sum_i (W_{ia} - W_{ib})^2 \quad (2)$$

The indices can be weighted as desired for increasing resolution. One approach is to define the indices as follows.

$$i(ab)^m = \sum \text{Abs value } (X_{ia} - X_{ib})^m / \sigma_i^n \quad (3)$$

where X_i is D_i or W_i or a mathematical combination thereof, σ_i is the standard deviation of X for the set of samples considered (at that wavelength) and each of m and n which are the same or different is weighting factor which is positive but can be a whole number or a fraction. Other variants can be used with other weighting factors such as those involving the spectral experimental error e_i , where e_i is the reproducibility of the spectral measurement at wavelength i . The choice between the different options for the weighted indices may be dictated by numerical efficiency.

The reproducibility of the experimental measurements in the standards may be at least 90% or 94% or 95%. The minimal index may be obtained from a reference standard samples set according to the following procedure, hereafter called the Minimal Index Procedure. The NIR spectra for 2 standard samples A and B and their property P e.g. Octane Number are determined. By means of equation (1), (2) or (3), the value of the proximity index i_{ab} is determined via the absorptions at a series of wavelengths; this index is applicable to the difference in properties $P_A - P_B$ called EP_{AB} . This

process is repeated with other pairs of standards c and d, e and f etc to obtain a series of Proximity Indices i_{cd} etc with corresponding property differences EP_{cd} etc. For different values of a parameter L which is greater than the indices i_{ab} etc, the corresponding values of EP_{ab} etc are averaged to give an average EP_j for that value of L; the different values of $EP_j + t\sigma/K$ are then plotted on a graph against L. σ is the accuracy of the property determination and K is the number of pairs of samples for which i_{ab} is inferior to a given L. t is the Student factor at a given level of confidence. The intercept is then measured between the curve obtained and a line usually horizontal which is the reproducibility of the property level at an appropriate confidence interval e.g. 90% or more usually 95%; the abscissa portion of the intercept gives the minimal index i_{min} , which is the minimum value of i_{ab} for which $P_a = P_b$ within the frame of experimental error.

From this minimal index by Procedure 1, the standards can be chosen which have values of $i_{ab} \leq i_{min}$ where in this case a is the unknown and b is a standard, as in this case the difference between Property a and Property b is less than or equal to $\sigma/2$, where σ is the experimental error in measuring the property. Then from the property P value or values of the chosen standard, the property of the unknown is obtained directly or by averaging those values, usually the arithmetic mean, but optionally with weighting.

The method of the invention may be used to determine more than one Property P at once, e.g. at least 2, such as 1-30 e.g. 2-10 properties at once. Each property of the standards has a particular unweighted, minimal index, which may lie in the region $0-10^{-10}$ e.g. 10^{-2} to 10^{-8} , in particular 5×10^{-7} to 5×10^{-4} . If the Minimal Index chosen is the smallest for all the properties desired, then the same one may be used for all the properties and the standards chosen will be suitable for all the properties. The Minimal Index for each property may be used separately, with different numbers of standards chosen for each property (assuming different Minimal Indices). If desired the same Minimal Index may be used, which is not the smallest, resulting in some of the chosen standards (with a higher Minimal Index) giving some properties of high accuracy and some (with a lower Minimal Index) giving some properties of less high accuracy.

The property to be determined may be of the sample being analyzed or a product obtained from that sample e.g. a product of blending or cracking the sample, as the property value obtained is derived from the standards, and they will have been determined as needed for the eventual use. Our EP304232 and 305090 referred to above describes such techniques when applied to use of NIR with correlation to blending or cracking operation; the same principles apply in the present method.

If the density of the standards in the data bank is sufficient to have $i_{ab} \leq i_{min}$ as is usually the case, the above procedure is very satisfactory. But there are occasions when the bank is incomplete, because of shortage of data of properties in a particular area i.e. a low density of standards or the sensitivity of the property to changes in absorption is so small, that a very small Minimal Index is required and there may be few standards with proximity indices meeting it. It is possible simply choose a larger Minimal Index with e.g. 1.5 times such as 1.5-2 times the Minimal Index; the results may be less accurate than those from a smaller minimal index.

However, a more accurate approach with a low density of standards involves a special densification process of Procedure 2, in which random or semi random densification of the neighbourhood of the unknown is achieved by generation of synthetic standards, based on standards already in the bank. Each new synthetic standard may be obtained from combinations of standards taken at random from the bank but preferably it is obtained from the other standards by the constraint of choosing only a mixture of N standards for which

$$(\text{Min})C_j - u_j \leq C_j \leq (\text{Max})C_j + u_j \quad (4)$$

$$\text{and } \sum C_j = 1 \quad (5)$$

where C_j is the fraction of component j in the sample.

$\text{Min } C_j$ is the minimum amount of j in the initial industrial calibration mixture or in the samples for which the method is to be used.

$\text{Max } C_j$ is the maximum amount of j in the initial industrial calibration mixture or in the samples for which the method is to be used.

u_j is usually between 1 and 0.01 preferably between 0.5 and 0.1 and can be fixed for each property.

The constraints over the choice of such mixtures of N standards can also be equally fixed in the spectral area from which the samples will be drawn in order to remain in the areas of similar chemical nature.

The number of samples effectively drawn into the bank in this densification can be of several thousand generally 1000-2000. The calculation time is extended without significant deterioration in the results. If no further neighbours are found, the trawl of new samples drawn in is enlarged.

The spectrum of each mixture is calculated by the combination of the spectra of the standards used according to the formula

$$S_{Mj} = \sum C_j \times S_j \quad (6)$$

where S_j is the spectrum in the mixture of component j in the calibration matrix.

The properties of each mixture PMI can be calculated by a generally linear combination of the properties of the standards according to the formula

$$P_{MI} = \sum C_{ij} \times P_j \quad (7)$$

where P_j is the property of component j

In the case of non linear additive properties, appropriate mixing factors can be applied e.g. by blending factors or similar for density and viscosity.

Having obtained the spectrum and the properties of the synthetic mixtures, these can be used as "standards" to help determine the properties of an unknown sample in the same way as a conventional standard.

Instead of using either of the two above approaches, 1-7, a third type Procedure 3 may be used as follows. The Q nearest samples to unknown X can be found from a selection from the bank samples for which the proximity index to the unknown sample is $(V) \times I_{min}$ where v is $0.1 < v < 10$, (8) preferably $0.5 < v < 2$ or $1 \leq v \leq 5$. Then by the method of least squares is found a generally linear combination of the standard products, which are the Q nearest samples to reproduce the spectrum of X according to the equation.

$$S_x = \sum C_R \times S_R \quad (9)$$

where C_r is the coefficient for sample R in the total Q and S_R is the spectrum of sample R. The coefficient C_R which can be normalized to $C_R = 1$ or not and/or optimized by the least squares route, allows an estimation of the property P_x according to the equation.

$$P_x = \sum C_R \times P_R \quad (10)$$

where P_R is the property of sample R.

The eventual size of the estimation error can be derived by application of Gaussian theory, also called the propagation error (see Eq.10).

The above third approach can only be applied if the product X is situated inside the maximum extensibility of the standard products defined by equation (8). If this is not the case, X is outside the field of the actual bank of products and escapes from the area of knowledge of the method into the area of learning.

The densification process described in relation to equations 4-7, or 9 or 10 is usually applied to the method of the invention involving no correlation or regression techniques. However, if desired the densification process may be applied to increase the number of "standards" for consideration in an NIR analytical technique involving the correlation on regression techniques as described above e.g. MLR. The present invention also provides a method for adding an extra synthetic standard to a bank of known standards, each of which relates at least one absorption in the 600-2500nm region (or derivative thereof) of a known material to a known property related to that material, which method comprises choosing from the bank at least 2 standards for which equations 4 and 5 above are met, considering mixing the chosen standards in at least one proportion to produce at least one mixture for use as a synthetic standard, and estimating the spectrum and property of said mixture according to equation 6 and 7 respectively.

The spectrum and property of each "mixture" can then be added to the bank and used to develop models through the known correlation/regression approach, e.g. as described in the above mentioned patents.

The method of the invention may be applied from the spectrum of a material to determine at least one physical, chemical, physicochemical and/or rheological property of that material, which may be a product of a chemical or physical or separation process, or which may be a feed to such a process, or the method can be used to determine at least one of said properties of a product of that process from the spectrum of at least one feed to that process, or to determine the yield of at least one product of that process. Each of the feed (or feeds) or products to the process may be a solid liquid or gas preferably at least one feed or product is a liquid.

Thus the method may be used for the physicochemical determination or prediction in relation to at least one feed or product used in or obtained by an industrial process of the refining of oil and/or in petrochemical operations. The process may be a hydrocarbon conversion or separation process, preferably a reforming or catalytic cracking or hydrotreatment process or distillation or blending. In particular it may be used for determination of at least one property of a feed and/or the prediction and/or determination of at least one property and/or yield of product from a number of different processes such as processes for separating petroleum products such as atmospheric distillation vacuum distillation or separation by distillation, under pressure greater than atmospheric, as well as thermal or catalytic conversion, with or without partial or total hydrogenation, of a petroleum product, such as catalytic cracking e.g. fluid catalytic cracking (FCC), hydrocracking, reforming, isomerization, selective hydrogenation, viscose reduction or alkylation.

Of particular value is the use of the method in blending operations involving the prediction and/or determination of at least one property of a blend of liquid hydrocarbons (optionally with other additives such as alkyl ethers or alcohols), this method including or not the determination for each constituent of the blend of a blend index for the property consid-

ered. In this method as applied to blending, the blend indices can be obtained simply by calculation and without the need for preparation of standard physical mixtures other than those contained in the databank. The blend indices can be combined linearly or non linearly within the fields of stability to determine from the value of this combination a value for at least one property of the blend obtained. The blend may be made by mixing at least 2 of butane, hydrogenated steamcracked gasoline, isomerate, reformate, oxygenates (MTBE, TAME, MeOH, TBA...), FCC derived gasoline. This process may be repeated with numerical addition of other constituents separately to the liquid hydrocarbon base to determine a series of blending indices and then determination from these indices of the properties of the multi constituent blend (see e.g. Ex. 2 hereafter).

Examples of properties that can be determined and/or predicted include the following: for automobile fuels/gasolines, at least one of the Research Octane Number (RON), Motor Octane Number (MON) and/or their arithmetic mean, with or without lead additive and/or the methyl tert, butyl ether or methyl isomethyl ether and/or benzene content:

For automobile fuels/gasolines, at least one of the vapour pressure, density, volatility, distillation curve, e.g. percentage distilled at 70°C and/or 100°C, oxygen content or benzene or sulphur content, chemical composition and/or gum content e.g. expressed in mg/100ml, and/or susceptibility to lead (these properties are particularly determined for use in blending operations):

For diesel fuels or gas oils, at least one of the cetane number (e.g. motor measured), cetane index, cloud point, "discharge point", filterability, distillation curve, density e.g. at 15°C, flash point, viscosity e.g. at 40°C, chemical composition, sensitivity to additives and percentage of sulphur;

For distillation products from crude oil e.g. under atmospheric pressure at least one of the density, percentage of sulphur, viscosity at 100°C, distillation curve, paraffin content, residual carbon content or Conradson carbon content, naphtha content, flash point for petrol, cloud point for gas oil e.g. light gas oil and/or viscosity at 100°C and/or sulphur content for atmospheric residues, and yield for at least one of the cuts, gasoline (bp 38-95°C), benzene (bp 95-149°C) naphtha bp 149-175°C, jet fuel bp 175-232°C, light gas oil bp 232-342°C, heavy gas oil bp 342-369°C, and atmospheric residue greater than 369°C.

For at least one of a feed or a product of a process of a catalytic cracking e.g. FCC process, at least one of the density, percentage of sulphur, aniline point, gas oil index, gasoline index, viscosity at 100°C, refractive index at 20°C and/or 50°C, molecular weight, distillation temperature e.g. 50% distillation temperature, percentage of aromatic carbon, content of total nitrogen and factors characterizing the suitability of the feed for the cracking e.g. KUOP, crackability factor, cokability factor, and yield e.g. of gas, gasoline, gas oil or residue. Thus there may be determined the yields and/or properties of the different products obtained by distillation of the cracked products, such as RON and/or MON, clear or leaded for the gasoline cut and the viscosity at 100°C for the distillation residue.

For at least one of a product or a feed of a catalytic reforming process, at least one of the density, distillation temperature and/or chemical composition (expressed as a percentage) of saturated linear hydrocarbon, isoparaffins, naphthenes, aromatics and olefins.

For at least one of a product or a feed of a process of hydrogenating gasoline at least one of the density, distillation temperature, RON and/or MON, clear or leaded vapour pressure, volatility, chemical composition (expressed as a percentage) of saturated linear hydrocarbons, isoparaffins, naphthenes, aromatics e.g. benzene, and mono/di substituted benzenes, olefins e.g. cyclic and non cyclic olefins, diolefins, the maleic anhydride index, and yield e.g. of at least one of the products obtained.

The method of the invention may also be used with chemical reactions in which at least one product is a hydrocarbon, and none of the feeds or products contains an element other than carbon or hydrogen. The hydrocarbon which may be gaseous or liquid at 25°C. Such reactions may involve as feed or product at least one olefin or acetylene e.g. linear or branched, aliphatic or cycloaliphatic olefin with an internal or external ethylenic unsaturation, preferably of 2-20 carbons especially 2-8 carbons for alkenes or alkynes (such as ethylene, propylene, butene 1 or 2, isobutene, isopentene) or acetylene, and 5-8 carbons for cycloalkenes e.g. cyclohexene. The feed or product may also be an aromatic hydrocarbon e.g. benzene or naphthalene, optionally substituted by at least one (e.g. 1-3) alkyl or alkenyl group e.g. of 1-20 carbons, such as 1-6 carbons, especially methyl, ethyl or isopropyl; examples are benzene, toluene, xylene, cumene and styrene. The feed or product may also be a non aromatic hydrocarbon, e.g. linear or branched aliphatic or cycloaliphatic with e.g. 1-20 or 5-8 carbons respectively, preferably 1-6 carbons and 6 or 7 carbons respectively, examples are methane, ethane, propane, n-butane, isobutane, and cyclohexane. The feed or product may also be a diene, conjugated or unconjugated, aliphatic or cycloaliphatic with e.g. 4-20 carbons or 6-20 carbons respectively; examples are butadiene and isoprene and cyclohexadiene. Examples of the reactions are hydrogenation (e.g. butadiene to butene-1 or 2 or cyclohexene to cyclohexane) dehydrogenation (e.g. ethane to ethylene or ethyl benzene to styrene), isomerisation (e.g. butene-1 or -2 to isobutene, or pentene-1 to isopentene) alkylation (e.g. benzene with ethylene to form ethylbenzene and/or styrene, or isobutene with butane to form iso octane), and cracking.

In addition to the use in petrochemical operations, the method is of wider application and may be applied in the pharmaceutical industry such as the production of pharmaceutically active compounds for use as medicines e.g. by fermentation, and in the perfumery industry for making perfumes and fragrances, especially in their blending and control thereof. The method may also be used in the food industry e.g. in brewing to control fermentation processes, in ferment-

tation to make wine and quality control thereof, and control of food production e.g. sugar and water content in fruit juice and in control of maturing processes for fruits and vegetables. In each case the method may be applied to determine a property of the sample tested or product from that sample e.g. a fermentation or blended product preferably on line and especially with continuous feed back from the results to control the production process.

In each of the above processes the property or yield of a product determined or predicted by the method of the invention can be compared to the desired figure and notice taken of any deviations by adjusting the parameters of the process e.g. proportion or nature of feed(s) and/or temperature/pressure etc to bring the property back to the desired figure. This control of the process, which may be a blending, separation or chemical process, is usually performed with a micro computer which is linked to the spectrometer and also performs the search for the standards S_m . The inline control of the process is very efficient and very fast.

The present invention also provides an apparatus suitable for carrying out the method of the invention comprising an infra red spectrometer and a computer wherein the infra red spectrometer is linked to the computer programmed in such manner that the property or yield may be determined continuously and in real time. The spectrometer is suitable for measuring spectra in the 600-2600nm wavelength range and can be linked to a signal processing device to allow numerical treatment of the spectrum, preferably by Fourier Transformation. The spectrometer receives at least one signal from a vessel containing product or from a feed or product line. The information obtained can be used as an information vector for the computer which is programmed to determine the property or yield e.g. via calculations on the proximity indices in relation to standards. Conveniently in relation to a process, the computer may be used in a closed loop feedback control system for controlling processing equipment e.g. changing the process parameters in response to variations in the property and/or yield of product from the desired value, from measurement of more than one absorptions in the NIR spectrum of the product and/or feed.

The benefits of invention allow improvements in modelling with the following areas. Identification and classification of novel products, simultaneous estimation of all of P properties on a sample without the need for generating P different models, and with the option of automatic upgrading of the model, the method being self learning or adjusting. The method of the invention overcomes the difficulties with the classical regression approach, in particular avoiding all difficulties with numerical stability of the models, allowing easy and rapid identification and classification of a sample of a product analyzed by spectral recognition and then instant conclusions as to whether the sample is known or unknown, allowing simultaneous determination of many properties and whether the property is simply additive or synergistic in relation to a blend composition; the latter is particularly useful for different blend indices and the indices considered.

The method also allows an extension of the field of application of the method without the need to rewrite the model, apart from the need to integrate the new samples which are inside or outside the previous field of validity of the method. This possibility of automatic learning, which is not possessed by traditional regression techniques, is a decisive advantage in the framework of continuous inline industrial control processes, because it allows the return of the industrial plant operations to the model in a certain and rapid manner in a minimum time and with all the properties considered in the model. In contrast classical regression methods would necessitate the redevelopment of all the models, which is long and laborious without being able to guarantee the result of the new model obtained, because a new validation period is necessary; in addition during the redevelopment of the model any commercial refinery use of the model is very limited. Furthermore, the method of invention allows equally the easy extension to a number of properties, which are simply incorporated into the known bank.

This remarkable possibility is true not only for conventional properties such as physical chemical and/or rheological properties, but also for complex ones (such as octane number). Also it is possible to quantify by the process the response or susceptibility to lead of automobile fuels as well as the response to additives such as nitrates, of fuels used in diesel engines. The methods of the invention equally allow application of the models from one apparatus to another and from one spectral region to another, where conventional regressive method cannot give satisfactory solutions. This apparatus portability is made possible by the fact that the differences between different spectra are the same in one apparatus as another, for the same type of spectrometer being considered (e.g. network scatter, Fourier transform, acousto optical system AOTS, diode array etc). This portability between spectral regions depends on the fact that as the spectral regions are intercorrelated, the relations between the spectra are maintained between one another.

The invention is illustrated in the following Examples in which the Minimal Index is calculated according to the Minimal Index Procedure described above. Mathematically the steps concerned are as follows.

For each couple of standard samples i, j , the Proximity Index i_{ij} is determined from the NIR spectra by use of equation 1, 2, or 3 and the properties are measured. For each Proximity Index is calculated the absolute difference EP_{ij} between the properties of the samples. The Minimal Index for property P is obtained from the average $(EM_p L)$ of EP_{ij} for different values of L when $L \geq ij$. Thus the $EM_p L = 1/K \sum \sum EP_{ij}$ for each of K samples for which $ij \leq L$.

$EMp(L)+to(M)$ is plotted against the proximity index and in addition there is plotted the reproducibility of the standard method at a given level of confidence, as defined in the Minimal Index Procedure above. The intercept of the curve from EMPL and the reproducibility give the upper limit i.e. the Minimal Index.

For the Examples the data is expressed in Tables in a form as shown below in which the data is as follows.

		Absorption				
		Weighting	Unknown	Estimated	Standard A	Standard B
Proximity Index						
Wavelength λ						
cm^{-1}	nm					
Property l						
Property j						
Property m						

The wavelengths chosen are shown in columns 1 and 2.

Column 3 gives the weight loading associated with each wavelength for the proximity index for the standards; 1 denotes no loading.

Column 4 shows for the unknown sample the absorption at the various wavelengths and at the bottom the properties of that sample determined by standard methods.

Column 5 shows for the unknown sample the estimated values of the properties and the absorptions using the method of the invention based on the properties and absorptions of the chosen standards.

Columns 6, 7 etc show the values of the absorptions and properties for the standards chosen from the bank. Line 2 give the value of the proximity index between the unknown sample and each of the chosen standards.

Example 1

Determination of Octane Number and other Properties of a Motor Fuel

The NIR spectra between 4800 and 4000cm^{-1} of a superfuel 1D and a number of standard superfuels of known properties were measured. The base line was taken at 4780cm^{-1} though similar results would be obtained with baseline drawn between 2 or more points. The absorbances were normalized.

By the Minimal Index Procedure described above, with use of equation 2 and non weighting of the absorbances the Minimal Index (MI) was calculated to be 1×10^{-4} . Following reference to the bank of data on superfuels and use of Procedure 1, 3 standard samples were found with a proximity index with respect to the superfuel of less than M1. The properties of these standards are shown in Table 1. From the properties of the standard samples, octane numbers (RON and MON), vapour pressure (hpa) volatility, percentage distilled at 70°C and at 100°C , gum content (in mg/ml), and content of sulphur, benzene (vol%) and MTBE were calculated for the superfuel by taking the arithmetic mean of the values for the 3 chosen standards. The estimated results are compared with the measured results.

All the properties were obtained from the single NIR measurement on the unknown superfuel and without any regression calculations, and with an accuracy in agreement with the reproducibilities of the reference methods. Other properties can be determined in a similar way.

Example 2

(a) Production of an Unleaded Mixed Fuel from 6 Components

A target SUPER98 superfuel of the properties given in column 3 of Table 2a1, was to be obtained by mixing the remains of a tank of finished gasoline with 5 components, butane, hydrogenated steamcracked gasoline HEN, isomerate ISOM, reformat (REF) and MTBE. NIR absorptions at 4800 – 4000cm^{-1} measured with a Fourier Transform spectrometer were measured, with a base line taken at 4780cm^{-1} and absorbances normalized. Results are in Table 2a1.

Mathematic calculations were done with a computer to mix the spectra and properties of the 6 components to reproduce a finished product.

5% MTBE (on target fuel) (i.e. 4-76% in the final mixture) was "added" mathematically to a spectrum of the target fuel to give a mixture whose NIR spectrum was noted. The Minimal Index was 1×10^{-4} determined as described above from the finished gasoline. 3 standards 2A, 2B and 2C were found with proximity indices with respect to the mixture, without weighting, and hence by averaging the properties of the standards the properties of the mixture were obtained. Table 2a.2 shows the spectrum of the mixture, the 3 standards and the estimation for the mixture as well as the properties of the standards and the estimated figures). The process was repeated with addition of each of the other 4 components to the spectrum of gasoline target.

On the basis of the figures obtained, the blending index for each property was found according to the linear formula

$$I^P(\text{mix}) = [(1+\alpha) \times P(\text{mix}) - P(\text{ref})] / \alpha$$

where $I^P(\text{mix})$ is the blending index for the ingredient in the mixture in relation to property P

α is the percentage of ingredient in the mixture

$P(\text{mix})$ is the property of the mixture (ingredient + gasoline) added) estimated by the process.

$P(\text{ref})$ is the property of the reference target gasoline.

The blending index for addition of MTBE is shown in Table 2a.3.

In order to obey the linearity law here, it is necessary to limit the additions to not more than a quarter of the minimum to maximum range of the constituent studied in the industrial mixtures. However for concentration less than 20% such as for these oxygenated compounds, addition of 5% is acceptable.

The process with MTBE added to the gasoline was repeated with the other 4 components (and on the basis of linearity in the blending as with MTBE) to obtain blending indices for them as well (see Table 2a.3). Then with the blending indices for each property for each ingredient, one can calculate the relative volume fractions needed to give the desired properties for the Superfuel 98 and hence the blending order. The 6 components were then mixed in the desired proportions and then properties of the mixture tested and compared to those estimated by the method of the invention from the components present (see Results in Table 2a.4). In the estimation of the products and the comparison with the bank of standards, the Minimum Index was 1×10^{-4} . 3 standards 2D, 2E, 2F were found with suitable proximity indices from which the properties of the superfuel were estimated by averaging as described in Procedure 1. There was good agreement between the properties obtained via the blending order, these measured on the fuel made and those estimated by the method of the invention. The differences are very small and in the area of reproducibility of the standard methods.

Example 2b

Production of a 5 component leaded Superfuel mixture

A target superfuel of the SUPER 97 type had with 0.15g/l of lead tetraethyl and having as specification an RON of 97, an NIR spectrum as in Col 3 of Table 2b1 below and other properties as given in col 3 of Table 2b1 below. There were available 4 components (HEN, 150M, REF and an FCC cat cracker gasoline) and the remains of a tank of finished refined gasoline for making the target fuel. The NIR spectra of these 5 components were measured as in Ex 2. The results are in Table 2b1.

As in Ex 2a, mathematical calculations were done with a computer to obtain the spectra and properties of 5 components to reproduce a finished product. Proximity indices with respect to standard samples were calculated based on normalized absorbencies which were not weighted. The method of the invention was used to find appropriate standards, using the procedure of artificial mixtures as described in Procedure 3 and equation 8 above in which v was 1 and with a Min. Index of 2×10^{-4} , the latter having been calculated for standard fuel mixtures as described above. Table 2b2 describes the results of addition of 5% of the FCC gasoline to a reference Super 97 gasoline target as well as the 3 standards 2G, 2H, 2J found by the method of this invention, from which the estimated properties were found. The same procedure was performed with the other components.

The blending indices were found in the same way as for Ex 2a, with the results for FCC gasoline in Table 2b3 and for the other components in the same way. The spectral blending index (for the linear area) is obtained for each property as shown in Table 2b3. A blending order was also calculated, as in Ex 2a, the results being in Table 2b3.

The process of Ex 2a was repeated but with the above components and a Minimal Index of 2×10^{-4} . The results are in Table 2b4.

3 standards 2K, 2L, 2M were found with appropriate proximity indices, which allowed the properties of the product to be estimated by averaging. Again good agreements is seen between the properties estimated from the blending order and those measured on the product made, and also between the same properties measured and those measured by the process. The differences seen are very small and in the area of reproducibility of the standard methods. Other properties can be obtained in a similar way.

Example 3Determination of cetane index and other properties of a gas oil

The properties of an unknown gas oil 3A were desired. The method of this invention was applied with respect to a bank of known standard gas oils with known NIR spectra. The NIR spectra were obtained by F T spectrometer in the $4800 - 4000 \text{ cm}^{-1}$ region [with 4780 cm^{-1} baseline and were normalized]. The proximity indices were calculated on the basis of Equation 2, and the Minimal Index was 2.5×10^{-6} (estimated from standard gas oil data as described above). The bank of standards was sufficiently dense for there to be found 2 standards 3B and 3C inside the sphere with proximity index less than 2.5×10^{-6} . Table 3.1 gives the details of the spectra and properties of the unknown oil A, and the standards and the estimated spectrum and properties, obtained by averaging. All the properties were obtained with an accuracy in agreement with the limits of reproducibility of the reference methods. Other properties can be obtained in a similar way.

Example 4

On line prediction, based on NIR spectra on a mixture of crude oils fed to an atmosphere distillation unit, of yields and properties of the different distillation cuts such as gasoline ($38-95^{\circ}\text{C}$) benzine ($95-149^{\circ}\text{C}$) naphtha ($149-175^{\circ}\text{C}$, jet fuel ($175-232^{\circ}\text{C}$) light gas oil ($232-242^{\circ}\text{C}$) heavy gas oil ($342-369^{\circ}\text{C}$) and atmospheric residue (top) 369°C).

An atmospheric distillation unit in a refinery was fed with a charge 4C which was a mixture in wt% of the following crudes, RUMASHKINO 81%, Iranian Heavy 18%, Iranian light 1%.

Yields of various distillation cuts were desired, the boiling ranges being given above, as well as key properties of each cut as described in Table 4.1, NIR spectra were measured as in Ex 1 on the crude oil. Min. Index was determined from NIR spectra on standard crude oil (as described above) and was 2.6×10^{-6} . The method of the invention was applied using Procedure 3 and equation 8, in which v was 1, to the bank which was sufficiently dense for 2 standards 4A and 4B to be found with small enough proximity indices. These standards contained (wt%) (for 4A) Romashkino 52% Iranian Heavy 29%, Arabian Heavy 11%, Kuwait 4%, Arabian light 2% and Iranian light 2% and (for 4B) Iranian Heavy 78%, Romashkino 21% and Arabian Heavy 1%. The data in Table 4.1 shows the observed properties as well as the yields of the cuts and their properties. The results obtained by this procedure were extremely satisfactory, the differences observed being in accordance with standard methods of measurement. Other properties can be obtained in a similar way.

The yields and properties of the distillation cuts remarkably were obtained directly on the basis of the NIR spectra of the feed and in line without regression type calculations.

Example 5Determination in line of the properties of a mixture of crude oils

Other properties of the charge mixture of crude oils of Ex 4 were sought, based on the NIR spectra determined as in Ex 4. The method of the invention was applied as in Ex 1 with the Minimal Index in all cases being 2.6×10^{-6} . Two standard crude petrols 4A and 4B were found in the bank by using Equation 2. The results are shown in Table 5.1. Other properties can be obtained in a similar way.

Here too the method demonstrates its capacity to predict all types of properties without any regression type of calculation requiring fastidious calculations. The results generally, as in the other Example, were in accordance with the results obtained by the reference methods, the deviations being found in the limits of reproducibility of the same methods.

Example 6Determination of the Properties of a feed to a reformer

A feed 6D to a reformer unit was analysed by the method of the invention as described in Example 1 with the NIR spectra recorded at $2000-2500 \text{ nm}$, the absorbancies normalised and not weighted. The NIR spectrum was compared by the method of Procedure 3 and equation 8 (wherein v is 1) with a Minimum Index of 2×10^{-4} , which had been previously calculated as described above from NIR spectra on standard reformer feeds. Three standards 6A, 6B and 6C from the reference feed bank were found with small enough proximity indices, details of the spectra of the feed and the standards are given in Table 6.1, together with 5 properties estimated for the feed by averaging the corresponding values of those standards. The actual properties of the feed were measured for comparison; the measurements were by traditional methods (gas chromatography and density), the former necessitating laboratory determination for several hours, compared to the present NIR process which gave the same results in a few minutes and on line (real time in the unit) and with better reproducibility.

The process allows the obtaining of a result with remarkable economy while avoiding having to produce 5 regressive models. The differences between the 5 properties as estimated and as measured experimentally are in agreement with the reproducibility of the known reference methods, namely 1.5% for gas chromatography for chemical compositions and 2% for density. The method can be equally applied for other properties such as ASTM distillation temperature curve for the feed.

Example 7

Determination of the properties of a feed to an FCC unit, as well as the yield and properties of the products obtained

The NIR spectrum of the above feed 7D was measured at $4800-4000\text{ m}^{-1}$, with base line at 4780 cm^{-1} , normalisation of the spectrum and no weighting. The procedure 3 was used with equation 8, with $v = 1$, and the Min. Index of 2.5×10^{-6} the latter having been previously calculated as described above from NIR spectra on standard FCC feeds of known properties.

The properties of the feed charge 7D sought were listed in Table 7.1 and included factors characterising the charge to the FCC unit, such as KUOP, crackability and cokability. The KUOP or Watson factor is defined as

$$\text{KUOP} = \frac{3}{\theta} \sqrt{\theta / \text{density } 60/60}$$

where θ is boiling point on a Rankin scale (Absolute Fahrenheit scale) and density 60/60 is the density of the feed at 60°F compared to that of water at 60°F.

The cracking unit operated under the following conditions: riser inlet temperature 250°C, riser outlet temperature 525°C, MHSV (Mass Hourly Space Velocity) 78 kg/h per kg, C/O ratio 6.6, activity of catalyst 65 (in Microactivity Test).

The cracking gave a gasoline cut defined by ASTM distillation with initial point of 38°C and 90% distilled at 190°C and a residue defined by ASTM distillation with 10% distilling at 385°C.

By application of Procedure 3 to the bank of samples of FCC feeds 2 standards were found namely 7A, 7B and the properties and yields estimated as shown in Table 7.1. The results were all in line with the accuracy based on the reference methods, as well as in line with the properties and yields actually measured. Other properties of the charge or products can be estimated in a similar way.

Example 8

On line determination of properties of the feed to a gasoline Hydrogenation unit.

The gasolines obtained from steam cracking units have the inconvenience of containing non negligible amounts of unsaturated dienic compounds, which have the effect of inducing and encouraging formation of gums which are undesirable in motor fuel. These gasolines are therefore selectively hydrogenated to eliminate the dienes without at the same time hydrogenating other unsaturated compounds present in the gasoline such as monoolefins and aromatics. The control over these dienes is therefore essential not only for the final quality of the fuel (principally RON and MON) but also for the hydrogen consumption of the hydrogenation unit.

Units for Hydrogenating gasolines from steamcrackers are generally coupled to a downstream distillation unit to separate a gasoline from a light cut (95% distillation by about 75°C) and one from a heavy cut (initial point about 95°C), before extraction of the benzene in the core cut and recycle of the extraction residue from that cut called raffinate.

It was desired to determine by the process of the invention the properties of the gasoline from the steam cracker, which was a feed to a gasoline hydrogenation unit. NIR spectra were obtained on the feed on line at 1000-1600 nm using a scatter dispersion spectrometer. The absorbances were normalised, but the data was not weighted for use in Equation 8, in which v was 1 and min was 2.5×10^{-5} (the latter having been determined from NIR spectra on similar feeds of known properties). 5 standards 8A-8E were found in the search using Procedure 3, and the properties of the feed calculated therefrom by averaging were all in agreement with the measured properties of the feed. The results are shown in Table 8.1.

In addition the chemical composition of the feed was obtained with great particularity allowing a distinction to be made for example between cyclic and non cyclic olefins as well as benzene and mono and di substituted aromatics. Equally by the process potential yields were obtained of the distillation cuts after the selective hydrogenation of the gasoline. All the properties were obtained with great accuracy within the limits of the experimental reproducibility for that kind of property.

Other properties can be determined such as Octane Indices for the different cuts or temperatures of ASTM distillation curves for the gasoline.

Example 9Method for use when the density of standards in the bank is insufficient

The MON level for a reformate 9A was sought. The NIR spectrum was measured at $4800\text{--}4000\text{ cm}^{-1}$ with a base line at 4780 cm^{-1} ; the spectra were normalised. With reference to NIR spectra on reformates of known properties the Minimal Index was found by calculation as described above to be 2×10^{-5} . The proximity indices of reformate 9A and known standards were determined by Procedure 1. The results were as given in Table 9.1. 5 standards 9B-F were found from the reformate bank with proximity indices low in relation to the reformate 9A, but insufficiently low to be less than Minimal Index, as the density of the bank was too small. It was thus not possible to calculate the properties with the accuracy desired. Procedure 1 using Equation 1 was replaced by Procedure 2 using Equations 4-7, with in Equation 4 values of C_j between -0.3 and +1.3, in order to increase the density of "standards" in the bank by providing new synthetic mixtures.

Tables 9.2 and 9.3 show the results obtained, showing in Column 3 the absorbancies and properties for the "standards" (MC1, MC2) obtained by this densification, and with small enough proximity indices. Col. 4 and subsequent columns give the absorbances properties of the standards 9B, 9D and 9G in the reformate bank used to generate the new "standards". Line 2 in these Tables show for each standard the fraction retained in the mixture to generate the new "standards". This fraction can be negative, but comprises between -0.3 (or -0.4) and +1.3 (in Eq.4).

Using the data on MC1 and MC2 as "standards", the properties of the reformate 9A were calculated by averaging (as shown in Table 9.4). The calculated MON of reformate 9A accords well with the experimentally measured figure, and is inside the limits of reproducibility of the standard method. The process can be used in a similar way for other properties.

The method of the invention equally allows immediate automatic upgrading of the bank by automatic integration of the new samples. The process with the proximity indices allows consideration as a standard of all the novel "standards" introduced into the bank. This property is remarkable because it allows very rapid determination of properties in the case of novel products not recognised in the bank and then the gaining of precious time in the adjustment of operating conditions for the manufacturing unit.

Table 9.5 shows that a novel "sample" measured immediately after incorporation of the above unrecognised sample 9A in the databank, now used as a standard, is recognised and is perfectly calculated for the totality of its properties and without any modification nor intervention on the used models. It is important to note the superiority of the procedure over classical regression models. The latter are incapable of predicting properties of samples not included within their application range or predict them with a non acceptable error, and therefore would need to be reactivated by the necessity to remake the model (one for each property) and this without guarantee of success, and with the commercial plant

functioning blind during the recalibration period.

TABLE 1.1
Determination of Octane Indices and other Properties in an automobile fuel

Proximate Index	Wavelength	Weighting	ID Measured	ID Estimated	IA	IB	IC
				0,00027524	0,00007452	0,000072577	0,000097807
λ (nm-1)	λ (nm)						
4720	2115	1	0,0021021	0,0021115	0,0021855	0,0020875	0,0020583
4740	2141	1	0,01555	0,016887	0,017029	0,015831	0,014801
4760	2155	1	0,01172	0,01464	0,017173	0,015595	0,015527
4785	2167	1	0,023425	0,022955	0,022671	0,022755	0,023429
4815	2181	1	0,014407	0,014779	0,014241	0,014853	0,014034
4845	2200	1	0,011377	0,011472	0,011516	0,011789	0,011112
4860	2242	1	0,015794	0,015825	0,015719	0,015331	0,014628
4905	2281	1	0,052392	0,050762	0,05071	0,052874	0,058701
4932	2308	1	0,127	0,12402	0,12292	0,1241	0,12505
4955	2325	1	0,10482	0,10478	0,1021	0,10946	0,10878
4970	2347	1	0,10001	0,099412	0,099621	0,09524	0,10409
4990	2375	1	0,065489	0,06726	0,067463	0,06664	0,06753
5010	2398	1	0,063954	0,06449	0,064634	0,064491	0,062546
5035	2418	1	0,064992	0,067348	0,065521	0,067075	0,069445
5055	2436	1	0,066511	0,066291	0,066551	0,064987	0,067336
5080	2463	1	0,10946	0,11196	0,11349	0,11337	0,10903
5090	2475	1	0,10273	0,10157	0,10554	0,10211	0,064659
RCN Clear			99,4	99,2	99	99,1	99,4
MCN Clear			88,4	88,2	88	88,1	88,4
TV Sps			700	705,0	710	715	690
Volatility			860	875,0	883	867	875
8Dist 100°C			58	54,7	54	58	52
8Dist 70°C			36,8	37	39	37	35
Resin			1,4	1,6	1,2	1,7	1,8
Sulphur			0,08	0,043	0,035	0,045	0,048
Headspace Vol			0,8	0,7	0,6	0,85	0,2
MTBE			5,6	5,8	6,7	6,3	5,5

TABLE 2a.1
NIR Spectra of Unleaded mixed fuel and base fuel and additives

		SUPER FUEL	BASE FUEL	BUTANE	MCN	ISOM	MTBE	REF
λ (nm-1)	λ (nm)							
4720	2119	0,0013833	0,0013284	0,00036614	0,0048746	0,00045176	0,00039505	0,0017699
4740	2141	0,015401	0,015198	0,00055139	0,035529	0,001807	0,00079685	0,02742
4760	2155	0,014458	0,014786	0,0015483	0,03355	0,0020854	0,0019907	0,025581
4785	2167	0,021629	0,021933	0,002432	0,048472	0,0033767	0,0013645	0,035613
4815	2181	0,011173	0,011556	0,0035046	0,026822	0,0032492	0,0043554	0,025327
4845	2200	0,010699	0,010705	0,013764	0,01651	0,0057573	0,013241	0,012712
4860	2242	0,015318	0,015446	0,015717	0,018958	0,010108	0,027911	0,0181
4905	2281	0,094023	0,094318	0,10437	0,061125	0,095255	0,13276	0,084676
4932	2308	0,12974	0,13081	0,14761	0,094076	0,1474	0,18122	0,11205
4955	2325	0,10626	0,10476	0,12279	0,093425	0,11981	0,03885	0,10927
4970	2347	0,10094	0,098981	0,11439	0,088133	0,11705	0,074657	0,090487
4990	2375	0,065672	0,065902	0,074313	0,054255	0,072316	0,091152	0,058607
5010	2398	0,065289	0,065063	0,057805	0,049511	0,074797	0,095725	0,05451
5035	2418	0,069147	0,068654	0,079862	0,046235	0,085847	0,063448	0,049256
5055	2436	0,068641	0,067702	0,069597	0,050826	0,082082	0,06768	0,052229
5080	2463	0,10677	0,10794	0,0875	0,12437	0,099589	0,076993	0,12989
5090	2475	0,10145	0,10197	0,083674	0,13189	0,079524	0,081235	0,10917
RCN Clear		99,1						
MCN Clear		88,2						
Vapour Pressure		31,74						
Volatility		905						
8Dist 100°C		49,93						
8Dist 70°C		34,4						

TABLE 2a.2
Effect of addition of MTBE on the Super Fuel

		Weighting	Mixture + 5% MTBE	Estimated	2A	2B	2C
ProxMity Index				0.000019059	0.00004957	0.000360618	0.000086413
A (cm-1)	Z (mm)						
4750	2119	1	0.0013362	0.0012751	0.0012748	0.0312691	3.0012645
4670	2141	1	0.0147051	0.014562	0.014384	0.014083	0.015219
4630	2155	1	0.013964	0.013804	0.014523	0.013557	0.013323
4615	2167	1	0.020795	0.02143	0.021489	0.021104	0.021698
4593	2181	1	0.012752	0.01255	0.012204	0.01312	0.012327
4483	2230	1	0.01082	0.010514	0.01341	0.01042	0.010712
4460	2242	1	0.015917	0.015594	0.016158	0.015226	0.015368
4335	2287	1	0.093888	0.094656	0.096107	0.09918	0.094711
4312	2308	1	0.13219	0.13256	0.1278	0.12911	0.13917
4305	2323	1	0.10425	0.10443	0.10689	0.10497	0.10142
4250	2347	1	0.099691	0.10039	0.10436	0.098324	0.098495
4210	2375	1	0.066885	0.066455	0.065544	0.065782	0.067039
4170	2398	1	0.066728	0.067485	0.065091	0.069061	0.068303
4125	2418	1	0.069823	0.071186	0.069457	0.07235	0.07175
4105	2432	1	0.327596	0.066773	0.055937	0.06758	0.0657
4050	2453	1	0.10535	0.10236	0.10385	0.101	0.10222
4040	2475	1	0.10049	0.10197	0.10152	0.10314	0.10126
		Reference supplies					
RON clear		99.1		99.6	99.7	99.5	99.5
MON clear		88.2		88.7	88.9	88.5	88.7
Vapour Pressure		731.74		718.8	711.2	720.0	725.2
Volatility		98.9		97.5	97.0	97.2	967.4
%Dist 100°C		49.93		52.3	52.0	54.0	50.8
%Dist 70°C		34.4		35.8	36.3	35.4	35.8

TABLE 2a 3

Blending Indices and Blending Order							
	(blending order)	Base Fuel	Butane	HEN	ISOM	MTBE	REF
Volume Fraction		19.30%	4.10%	31.70%	32.10%	5.60%	7.2%
RON clear	99.4	100.2	97.5	103.6	93.0	109.6	100.7
MON clear	88.2	88.0	88.5	88.0	86.7	98.7	88.42
Vapour Pressure	709.1	767.0	4700.0	98.7	923.0	460	208.2
Volatility	972.4	975.0	5000.0	212.0	1430.0	718.3	177.3
%Dist 100°C	54.9	50.2	200.0	-5.0	97.5	99.7	24
%Dist 70°C	37.8	31.3	142.8	-12.9	84.2	63.8	-8.3

TABLE 2a.4
Comparison of the result obtained via the blending order and those of the product obtained

		Weight	Proton		2D	2E	2F
Proximity Index			Made	Estimated			
				0.600027526	0.000047452	0.300072577	0.000096607
λ (nm)	λ (nm)						
4720	2115	1	0.0021031	0.0021115	0.0021985	0.0020678	0.0020683
4670	2141	1	0.016494	0.016887	0.017029	0.015831	0.015801
4640	2155	1	0.016172	0.016464	0.017171	0.015625	0.015627
4615	2167	1	0.022425	0.022595	0.022471	0.022765	0.023429
4585	2181	1	0.014407	0.014379	0.014241	0.014853	0.014014
4485	2230	1	0.011377	0.011472	0.011516	0.011788	0.011112
4440	2242	1	0.015794	0.015825	0.015719	0.015321	0.015428
4385	2281	1	0.052392	0.090762	0.09071	0.092874	0.089701
4332	2308	1	0.127	0.12402	0.12592	0.1241	0.12505
4305	2323	1	0.10482	0.10679	0.10621	0.10945	0.10879
4250	2347	1	0.10001	0.099412	0.098621	0.095524	0.10409
4210	2375	1	0.055489	0.06726	0.067463	0.064664	0.067653
4170	2398	1	0.043954	0.06440	0.064434	0.064491	0.062566
4135	2417	1	0.057348	0.065348	0.065523	0.057075	0.069445
4105	2448	1	0.066511	0.066291	0.066551	0.064957	0.067336
4050	2463	1	0.10946	0.11196	0.11349	0.11337	0.10903
4040	2475	1	0.10273	0.10157	0.10564	0.10211	0.096959
(blending order)			Measured standards				
ECN clear	99.4		99.4	99.2	99	99.3	99.4
MCN clear	88.2		88.4	88.2	88	88.1	88.4
Vapour Pressure	709.1		700	705.0	710	715	690
Volatility	972.4		980	975.0	983	967	975
1Dist 100°C	54.9		58	54.7	54	58	52
1Dist 70°C	37.8		36.8	37	39	37	35

TABLE 2b.1
NMR spectrum of Target Super Fuel, and base stocks available

λ (nm)	λ (nm)	Target		Gasoline		FCC		HDS		ISOM		REF	
4320	2119	0,0014234	0,001295	0,0029238	0,0045938	3,0004093	0,001657						
4370	2141	0,0052428	0,000594	0,005967	0,037011	3,0022427	0,024442						
4400	2155	0,0052599	0,00908	0,0048202	0,033868	3,0021945	0,023848						
4415	2167	0,013234	0,012989	0,0052342	0,046361	3,0035967	0,032231						
4585	2181	0,0098247	0,0066662	0,0077879	0,028857	3,0033395	0,023754						
4485	2230	0,010777	0,010379	0,014512	0,015496	3,0059411	0,022231						
4440	2242	0,014409	0,014075	0,016828	0,018139	0,0102	0,017515						
4385	2281	0,093239	0,093239	0,095498	0,078898	0,095201	0,085552						
4332	2308	0,14045	0,1408	0,1543	0,092697	0,14681	0,11852						
4305	2323	0,12095	0,12095	0,13213	0,091686	0,11947	0,11079						
4250	2347	0,11073	0,11062	0,11559	0,086428	0,11763	0,093562						
4210	2375	0,068913	0,069012	0,073406	0,052861	0,072136	0,060461						
4170	2398	0,069683	0,069948	0,073798	0,049022	0,075191	0,057775						
4135	2417	0,071227	0,071735	0,067143	0,045077	0,085471	0,05255						
4105	2436	0,070003	0,070833	0,065603	0,050963	0,082203	0,056178						
4050	2463	0,10201	0,10185	0,099357	0,13909	0,095705	0,1243						
4040	2475	0,084489	0,08458	0,0697	0,1286	0,079381	0,10459						
ECN clear	97,5		97,5										
MCN clear	86,2		86,2										
Vapour Pressure	696		696										
Volatility	605,4		605,4										
1Dist 100°C	62,54		62,54										
1Dist 70°C	42,24		42,24										

TABLE 2b.2
Effect of addition of 5% FCC gasoline on Super 97 Product

Approximate index Wavelength	Weight λ (nm)	Mixture		2G	2H	2J
		Actual	Estimated			
			3.41E-05	5.77E-05	5.53E-05	7.98E-05
λ (nm-1)	λ (nm)					
4750	2115	1	0.001495	0.001415	0.001411	0.001414
4870	2141	1	0.009125	0.008837	0.008658	0.008758
4640	2155	1	0.009144	0.008948	0.00901E	0.008955
4615	2167	1	0.013045	0.012691	0.012631	0.013035
4545	2181	1	0.009719	0.009605	0.009454	0.009482
4485	2230	1	0.010955	0.010851	0.010639	0.010909
4460	2242	1	0.014524	0.014847	0.01487	0.014917
4385	2281	1	0.091432	0.094816	0.094259	0.096722
4372	2309	1	0.111111	0.11368	0.114703	0.11759
4305	2323	1	0.12149	0.12506	0.12261	0.12559
4250	2347	1	0.11056	0.11021	0.11119	0.11141
4210	2375	1	0.069127	0.06648	0.066776	0.065499
4170	2398	1	0.06969	0.068945	0.067881	0.069493
4135	2418	1	0.071032	0.070704	0.069102	0.072335
4105	2436	1	0.069765	0.069612	0.071511	0.069153
4070	2473	1	0.1314	0.13015	0.13061	0.131
4040	2475	1	0.083765	0.081801	0.082343	0.092854
	Reference SUPER97					
RON clear	91.9			97.6	97.7	97.5
MON clear	86.2			85.9	86.1	85.7
Vapour Pressure	590			586.1	590.0	584.2
Volatility	905.4			892.2	901.0	887.5
%Dist 100°C	52.54			62.3	62.8	61.4
%Dist 70°C	42.24			41.7	42.5	41.7

In this Table 3.41E-05 means 3.41×10^{-5}

TABLE 2b.3

Blending Indices and Blending order						
Volume Fraction	(blending order)	Gasoline	FCC	HEN	ISOM	REF
		12.93%	31.85%	8.46%	37.55%	9.20%
RON clear	97.7	97.9	91.6	101.1	101.5	100.
MON clear	86.3	86.4	79.9	83.5	92	87.9
Vapour Pressure	589.9	648.0	388.1	137.7	930.0	235.0
Volatility	952.7	968.5	628.2	274.2	1559.0	204.7
%Dist 100°C	65.5	63.2	57.5	6.3	96.0	26.4
%Dist 70°C	45.4	43.1	30.9	-10.7	83.3	-4.3

TABLE 2b.4
Comparison between the results from the blending order and the product obtained

Proximity Index	Weight	Measured	Product		2K	2L	2M
			Measured	Estimated			
				3.41E-05	5.33E-05	0.000159	0.000159
λ (cm-1)	λ (nm)						
4750	2119	1	0.001742	0.001809	0.001775	0.001851	0.001802
4570	2141	1	0.009508	0.009166	0.009131	0.009122	0.009104
4540	2155	1	0.008698	0.00926	0.009329	0.009695	0.008759
4515	2167	1	0.012758	0.013206	0.012772	0.013574	0.01327
4585	2181	1	0.009725	0.009549	0.009542	0.009921	0.009484
4485	2230	1	0.010459	0.010438	0.010498	0.010336	0.010491
4460	2242	1	0.014142	0.014252	0.014878	0.013896	0.013962
4385	2281	1	0.050899	0.093317	0.092897	0.09338	0.093476
4332	2309	1	0.13655	0.13974	0.13452	0.13589	0.14683
4305	2323	1	0.1596	0.12103	0.1195	0.1248	0.11879
4260	2347	1	0.11495	0.1128	0.11271	0.11215	0.11352
4210	2375	1	0.071524	0.068713	0.071255	0.068118	0.066566
4170	2398	1	0.070662	0.070304	0.069555	0.069388	0.071649
4135	2418	1	0.072077	0.071069	0.070001	0.07464	0.069566
4105	2436	1	0.069445	0.071756	0.07371	0.071075	0.070922
4050	2463	1	0.10444	0.10055	0.10143	0.098515	0.10269
4040	2475	1	0.086116	0.08264	0.084447	0.081297	0.079575
(blending order)			Measured standards				
BON clear	97.7		97.5	97.7	97.8	97.5	97.7
MCN clear	86.3		86.4	86.2	86	86.1	86.5
Vapour Pressure	589.9		593	598.0		600	598
Volatility	952.7		949	956.7		955	955
Dist 100°C	65.5		62	63.0		64	60
Dist 70°C	45.4		47	44.2		42	44

TABLE 3.1
Determination of cetane index and other properties of a gas oil

Proximity Index	Weight	Measured	Gas Oil A		3B	3C
			Measured	Estimated		
				1.71E-66	1.39E-05	2.23E-06
λ (cm-1)	λ (nm)					
4750	2118.6	1	0.000120383	0.000126618	0.000139425	0.000113411
4572	2140.4	1	0.001942853	0.002013913	0.002015876	0.002011949
4540	2155.2	1	0.003434747	0.003415109	0.003438675	0.003399343
4616	2166.4	1	0.004544314	0.004490759	0.004476561	0.004505037
4584	2181.5	1	0.004729896	0.0046754	0.00463465	0.004715149
4484	2230.2	1	0.007115983	0.006932337	0.006908771	0.006955903
4450	2246.2	1	0.010549409	0.010133388	0.010064553	0.010202122
4394	2281	1	0.07460604	0.074825207	0.074930117	0.074820298
4332	2308.4	1	0.158477852	0.157745031	0.15799051	0.157499551
4304	2323.4	1	0.101824835	0.102266697	0.102217602	0.102315793
4260	2347.4	1	0.131871507	0.131331453	0.131380548	0.131282357
4208	2376.4	1	0.088427865	0.088637684	0.08855913	0.088716237
4168	2399.2	1	0.092899205	0.093012126	0.093105408	0.092918844
4132	2420.1	1	0.084503812	0.08475911	0.084627844	0.084690376
4104	2436.6	1	0.081106377	0.081297851	0.081361676	0.081234027
4050	2463.1	1	0.08642837	0.086487285	0.086487285	0.086487285
4040	2475.2	1	0.067192608	0.06740372	0.067418449	0.067388991
Cetane Index			52	52.5	53.3	51.7
Cetane Number			55.3	52.75	62.1	53.4
Density 15°C			0.8434	0.84085	0.8385	0.8432
Flash Point			42	57.5	60	55
% sulphur			0.29	0.25	0.23	0.27
Cloud Point			5.1	5.5	5	6
Filtrability			1	0.5	1	0
Viscosity 40°C			3.1	3.7	3.7	3.7

TABLE 4.1
Determination of yields and properties of cuts from distillation of mixture of crude feed oils

	Weight		Charge 4C		4A	4B
	Proxymity Index		Measured	Estimated		
				9,98E-07	1,21E-06	1,33E-05
	λ (cm-1)	λ (nm)				
4572	2140.4	1	0.001777942	0.001748627	0.001771733	0.00172552
4440	2155.2	1	0.001139917	0.003211964	0.003252111	0.003167717
4616	2166.4	1	0.00377911	0.003827795	0.003835639	0.003819552
4584	2191.5	1	0.003794844	0.003139791	0.003829737	0.003769845
4484	2230.2	1	0.002094959	0.00614454	0.006272381	0.006016194
4460	2242.2	1	0.405258476	0.009155818	0.009276757	0.009034879
4384	2281	1	0.073089814	0.077898738	0.077657015	0.078120457
4332	2308.4	1	0.15773336	0.157794497	0.157793411	0.157795534
4304	2323.4	1	0.104631107	0.1045241	0.104179068	0.104869135
4260	2347.4	1	0.130690546	0.130249322	0.130445176	0.13053468
4208	2376.4	1	0.087815393	0.087751054	0.087838988	0.08766312
4172	2396.9	1	0.091208017	0.090879369	0.090878774	0.090880025
4132	2420.1	1	0.084648925	0.084706329	0.08465164	0.084761019
4104	2436.6	1	0.0824855	0.082364069	0.082389011	0.082340562
4060	2453.1	1	0.087068028	0.087578898	0.087475	0.087582795
4040	2475.2	1	0.067784043	0.068366138	0.068439445	0.068292927
Density 15°C			0.8663	0.86555	0.8646	0.8665
% Gasoline			7.4	7.4	7.4	7.4
% Kerosene			7.5	7.2	7.3	7.2
% Naphta			4.3	4.3	4.3	4.3
% Petrol			3.5	8.5	8.5	8.4
% light gas oil LGO			13.9	18.0	19.2	16.5
% Heavy gas oil			4.5	4.5	4.5	4.4
% Residue RMT			49	49.2	48.6	49.8
% Paraffines Naphta			52.2	52.1	53.1	51.2
Flash Point Petrol			59.2	59.5	59.4	59.3
Cloud point LGO			-3.1	-8.1	-8.0	-7.5
% Sulphur RMT			2.8	2.8	2.3	2.9
Viscosity 100°C RMT			53.10	52.72	48.53	56.71

TABLE 5.1
On line determination of properties of a mixture of crude oils

		Weight	Mixture 4C		4A	4B
	Proximity Index		Measured	Estimated	1, 04E-06	1, 27E-06
λ (cm-1)	λ (nm)					
4672	2140,4	1	0,001777942	0,001747949	0,001771058	0,00172484
4640	2155,2	1	0,003139917	0,00321072	0,003254971	0,003164468
4616	2169,4	1	0,00377911	0,003826312	0,003834119	0,003818445
4584	2181,5	1	0,003794844	0,003796319	0,003828299	0,00374436
4484	2230,2	1	0,006094959	0,006142161	0,006269999	0,006014322
4460	2242,2	1	0,009258476	0,009152272	0,009273227	0,009031317
4384	2281	1	0,078089814	0,077868554	0,077637461	0,078099647
4332	2308,4	1	0,15773336	0,15773336	0,15773336	0,15773336
4304	2323,4	1	0,104631107	0,1044836	0,104139419	0,104827782
4260	2347,4	1	0,130690546	0,130198858	0,130395533	0,130002183
4208	2376,4	1	0,087815393	0,087717055	0,087805559	0,087628552
4172	2396,9	1	0,091208037	0,090844188	0,090844188	0,090844188
4132	2420,1	1	0,084648925	0,08467351	0,084619424	0,084727595
4104	2436,6	1	0,0824855	0,08233077	0,082357661	0,082308493
4060	2463,1	1	0,087068029	0,087544965	0,08744171	0,087446219
4040	2475,2	1	0,067784043	0,06833965	0,068414403	0,06825897
Density			0,8663	0,86555	0,8646	0,8665
% Sulphur			1,6	1,65	1,6	1,7
Viscosity 100°C			2,27	2,265	2,36	2,17
% Conradson Carbon			4,8	5	4,8	5,1
% Paraffin content			5	4,95	4,9	5

TABLE 6.1

Determination of the Properties of a reformer feed						
	Weight	Feed 6D		6A	6B	6C
		Measured	Estimated			
Proximity Index				5,7E-4	8,2E-5	9,7E-5
λ (nm)						
2210	1	0,04624	0,04659897	0,04648	0,04671	0,04659
2260	1	0,18118	0,18154437	0,18233	0,18132	0,18085
2266	1	0,25391	0,25482278	0,25605	0,25439	0,25386
2276	1	0,33866	0,33942652	0,3412	0,33844	0,33857
2286	1	0,33776	0,33747772	0,3395	0,33634	0,33652
2307	1	0,54602	0,54558172	0,54286	0,54922	0,54375
2328	1	0,38819	0,38770261	0,38812	0,38791	0,38685
2344	1	0,4557	0,4561672	0,45568	0,45592	0,45717
2376	1	0,31751	0,31727184	0,31483	0,32067	0,31543
2397	1	0,33674	0,33644352	0,33466	0,33858	0,33561
2408	1	0,31787	0,31746329	0,31737	0,31904	0,31525
2418	1	0,32524	0,32334235	0,3244	0,32341	0,32186
2437	1	0,34758	0,34790932	0,34915	0,34543	0,34996
2457	1	0,38142	0,38057046	0,3793	0,38076	0,38195
% Linear Saturated		33,0	32,6	32,5	32,4	32,9
% Isoparaffins		30,1	30,8	31,4	31,1	29,9
% Naphthenes		29,3	29,2	29,2	28,5	30
% Aromatics		7,6	7,4	6,9	8	7,2
Density		0,7151	0,7158	0,7152	0,7167	0,7155

TABLE 7.1
Determination of Properties of feed to FCC reactor and yields and properties of products

	Proximity Index	Weight	Feed ID		7A	7B
			Measured	Estimated		
				1,10E-06	1,28E-06	1,30E-06
λ (cm-1)	λ (nm)					
4120	2418,5	1	0,00024017	0,000283004	0,000238346	0,000327662
4572	2140,4	1	0,002238801	0,002010344	0,001890879	0,002135985
4640	2155,2	1	0,004237324	0,003903227	0,003874117	0,003932335
4612	2168,3	1	0,005237444	0,004972647	0,004866233	0,005079102
4584	2181,5	1	0,005332797	0,005055095	0,005031089	0,005079102
4484	2210,2	1	0,007970687	0,007756354	0,007744263	0,007768446
4460	2242,7	1	0,011303264	0,011210967	0,011212199	0,011209736
4384	2281	1	0,072994655	0,07273491	0,07252198	0,072545839
4332	2308,4	1	0,152067443	0,152159348	0,151545649	0,152373047
4304	2323,4	1	0,100517606	0,100397569	0,100601923	0,100193214
4250	2347,4	1	0,131209247	0,131514201	0,131487607	0,131540794
4212	2374,2	1	0,091618024	0,091623192	0,091564633	0,091681751
4116	2399,2	1	0,094011773	0,094362962	0,09427582	0,094370104
4132	2420,1	1	0,08194908	0,086675314	0,086677538	0,08667209
4104	2436,5	1	0,081457005	0,081916022	0,081981133	0,081850912
4050	2463,1	1	0,084267922	0,084318052	0,084444043	0,08419206
4040	2475,2	1	0,06911082	0,059146752	0,069239547	0,069053957
Density			0,926	0,9225	0,922	0,923
1 Sulphur			1,97	1,85	1,83	1,87
Aniline Point			83,5	83,2	78,2	88,2
Viscosity 100°C			8,8	9,1	8,7	9,5
Temp. 50% distilled			461	464	457	471
ROGP			11,8	11,85	11,8	11,5
Mol. Weight			450,6	449,95	434,5	465,4
1 Aromatic Carbon			21,8	21,2	21,6	20,5
CRACKABILITY			2,47	2,57	2,55	2,55
CONVAILITY			1,01	1,00	0,99	1,01
GASOIL INDEX			1,55	1,515	1,54	1,45
GASOLINE INDEX			0,99	0,985	0,99	0,98
Gasoline Yield (%)			45	44,5	43	46
Residue Yield (%)			12	11,25	13	9,5
RON Clear Gasoline			92,7	92,4	92,4	92,4

TABLE 8.1
On line Determination of properties of feed to hydrogenation unit for gasoline(?)

	Peak Index	Weight	Feed EF		SA	SB	SC	SD	SE
			Measured	Estimated					
				0,000042	0,000034	0,000047	0,000014	0,000130	0,000922
	λ (cm-1)	λ (nm)							
8	8749	1117,5	1	0,00443	0,004553	0,004082	0,00455	0,004137	0,004503
9	8795	1127	1	0,036107	0,035349	0,035282	0,035954	0,035429	0,035343
10	8780	1130	1	0,035287	0,0349	0,035551	0,036992	0,036513	0,036491
11	8784	1141	1	0,040895	0,040523	0,040341	0,040715	0,040315	0,040077
12	8773	1146,5	1	0,039495	0,039004	0,039152	0,039435	0,038441	0,038923
13	8688	1151	1	0,027962	0,027743	0,027983	0,028106	0,027183	0,027774
14	8673	1153	1	0,024452	0,024293	0,024501	0,024562	0,023745	0,024321
15	8551	1156	1	0,020612	0,020535	0,02067	0,020691	0,020084	0,020403
16	8611	1160	1	0,018274	0,018283	0,018339	0,018365	0,018349	0,018385
17	8576	1166	1	0,01793	0,018054	0,018108	0,017858	0,018142	0,01814
18	8555	1167,5	1	0,018035	0,018177	0,018257	0,017527	0,018321	0,018248
19	8525	1173	1	0,018845	0,019053	0,019164	0,018622	0,019265	0,019051
20	8494	1177	1	0,020412	0,020832	0,020937	0,020311	0,021058	0,02094
21	8466	1184	1	0,0274	0,027769	0,027082	0,027136	0,028172	0,028072
22	8419	1189	1	0,031415	0,031149	0,031306	0,031481	0,032525	0,032571
23	8395	1192	1	0,033452	0,03402	0,033845	0,033563	0,034457	0,034442
24	8347	1195	1	0,031083	0,031458	0,031409	0,031279	0,031529	0,031497
25	8326	1201	1	0,028705	0,029172	0,029055	0,029164	0,029138	0,028993
26	8313	1203	1	0,027931	0,027733	0,027583	0,027324	0,027708	0,027492
27	8285	1207	1	0,024959	0,0251	0,02483	0,025172	0,025132	0,024829
28	8264	1210	1	0,022844	0,022933	0,022777	0,022977	0,023009	0,022646
29	8203	1213	1	0,019306	0,019327	0,019374	0,019523	0,019542	0,019009

TABLE 8.1 (cont)
On line Determination of properties of feed to hydrogenation unit for gasoline(?)

	Peak Index	Weight	Feed EF		SA	SB	SC	SD	SE
			Measured	Estimated					
				0,000042	0,000034	0,000047	0,000014	0,000130	0,000922
	λ (cm-1)	λ (nm)							
30	8140	1228,5	1	0,00894	0,0089634	0,009101	0,008848	0,009078	0,008757
31	8065	1240	1	0,004327	0,004406	0,004447	0,00427	0,004391	0,00421
32	7958	1269	1	0,000897	0,0009398	0,000895	0,00094	0,000918	0,000921
33	8117	1232	1	0,005349	0,0054614	0,005304	0,005521	0,005209	0,005233
34	7824	1247	1	0,008089	0,008052	0,008054	0,008116	0,008437	0,008101
35	7996	1252	1	0,012205	0,012095	0,012056	0,012119	0,01192	0,012269
36	7380	1355	1	0,015806	0,015764	0,015674	0,015614	0,015488	0,015136
37	7356	1359,5	1	0,022613	0,022831	0,022693	0,022499	0,022515	0,022452
38	7349	1361	1	0,024481	0,024925	0,024783	0,024423	0,025031	0,024538
39	7339	1362,5	1	0,026435	0,026707	0,026552	0,026428	0,026418	0,026438
40	7321	1364	1	0,029615	0,029773	0,02975	0,02954	0,029849	0,030217
41	7273	1375	1	0,038104	0,038252	0,038215	0,037747	0,038738	0,038761
42	7254	1378,5	1	0,042097	0,042367	0,042333	0,041789	0,042404	0,04293
43	7241	138	1	0,044261	0,044511	0,044521	0,043951	0,044955	0,045039
44	7231	1381	1	0,045451	0,045555	0,045635	0,045014	0,045882	0,045992
45	7159	1389	1	0,04633	0,046274	0,046333	0,045746	0,046004	0,04583
46	7124	1392	1	0,046961	0,0469347	0,046942	0,046812	0,046816	0,046557
47	7161	1396,5	1	0,049514	0,0495104	0,049526	0,049149	0,049522	0,0495214
48	7151	1398,5	1	0,04693	0,046706	0,046937	0,046708	0,046735	0,046854
49	7117	1409	1	0,0471	0,04703	0,047033	0,046925	0,046446	0,046455
50	7105	1407,5	1	0,046793	0,046838	0,046789	0,046579	0,046484	0,046242
51	7087	141	1	0,045855	0,046047	0,045894	0,045986	0,045829	0,045454

TABLE 8.1 (cont)

On line Determination of properties of feed to hydrogenation unit for gasoline(?)

Prox. Index	Weight	Feed SF	JA		SF		SC		SD		SE						
			Measured	Estimated	0.0000042		0.0000034		0.0000047		0.0000114		0.0000130		0.0000222		
A (cm-1)	λ (nm)																
7070	1414.5	1	0.043481	0.043602	0.043573	0.04322	0.043476	0.043002	0.043138								
7018	1425	1	0.036493	0.036481	0.036552	0.036241	0.036396	0.035533	0.035784								
6991	1430.5	1	0.037445	0.037372	0.037024	0.0375	0.037441	0.03717	0.037274								
6974	1434	1	0.037514	0.037391	0.037162	0.037605	0.037362	0.037265	0.037298								
6971	1434.5	1	0.037367	0.037261	0.03706	0.037466	0.037496	0.037135	0.037127								
6930	1443	1	0.032307	0.032112	0.032218	0.032451	0.032217	0.031884	0.03179								
6845	1460	1	0.022124	0.021997	0.022177	0.022295	0.022105	0.021462	0.021565								
6824	1465.5	1	0.021591	0.021377	0.021682	0.021745	0.021593	0.021154	0.020925								
6752	1481	1	0.018013	0.01796	0.018203	0.018411	0.017735	0.017774	0.017678								
6725	1488	1	0.016091	0.016058	0.016257	0.016607	0.015759	0.015855	0.015811								
6493	1494	1	0.014581	0.014542	0.014741	0.015042	0.014336	0.01435	0.014215								
6414	1512	1	0.010568	0.01045	0.010546	0.011075	0.010321	0.010393	0.010114								
6344	1523	1	0.007881	0.007804	0.007827	0.008432	0.007533	0.007562	0.007658								
6334	1530	1	0.007116	0.007114	0.007111	0.007273	0.006783	0.006993	0.006957								
6181	1593	1	0.005233	0.005264	0.005299	0.005895	0.004821	0.005154	0.005153								
			GA 412	Est-time		JA 416	GA 421	GA 406	GA 420	GM 452							
λ Linear Saturated			8.73	8.96		7.73	7.98	10.65	8.86	8.59							
λ Isoparaffins			6.83	7.35		6.51	6.62	8.5	8.26	8.56							
λ Naphthenes			5.83	5.73		6.38	6.93	6.95	4.97	4.95							
λ Linear Olefins			11.33	11.92		12.41	12.49	10.49	11.13	11.28							
λ Cyclic Olefins			12.79	12.77		12.99	13.48	12.94	11.81	12.44							
λ Benzene			22.44	21.74		21.35	21.38	21.34	21.53	21.1							
λ Toluene			13.72	13.63		13.71	13.51	13.55	13.18	14.18							
λ Xylene			5.08	5.74		5.57	5.57	4.89	11.36	5.5							
λ Alkyl Benzene			5.56	5.94		5.98	5.6	5.11	6.94	6.25							
λ Dienes			16.44	15.50		17.67	17.94	14.83	13.57	15.47							
ODCITY			0.8174	0.8066		0.8133	0.8097	0.8012	0.803	0.8058							
Yield light cut			25.7	25.7		24.6	25.1	28.5	27.5	28.0							
Yield heavy cut			40.3	39.4		41.7	41.2	35.7	39.7	38.7							
Yield raffinate			13.7	13.3		13.5	13.4	13.7	12.4	13.5							
Yield benzene			20.3	20.6		20.2	20.3	22.1	20.4	20.0							

TABLE 9.1
Determination of MON of a reformate

Proximity Index	Weight		Reformat 9A		9B	9C	9D	9E	9F
	λ (cm-1)	λ (nm)	Measured	Estimated	0.0000638	0.0000638	0.0001815	0.0001852	0.0001985
			0.0010584						
4720	2119	1	0.0010583	0.0012043	0.0012355	0.0007601	0.0010861	0.0001935	
4670	2141	1	0.017444	0.018781	0.018911	0.014737	0.01556	0.015581	
4640	2155	1	0.018144	0.019076	0.019076	0.016358	0.014281	0.01559	0.015344
4615	2167	1	0.024297	0.025324	0.021903	0.019435	0.023444	0.021006	
4585	2181	1	0.020715	0.020612	0.017659	0.016021	0.016114	0.016429	
4485	2236	1	0.012119	0.011885	0.011415	0.010242	0.01136	0.010522	
4460	2242	1	0.018197	0.017086	0.016221	0.015362	0.016719	0.015344	
4385	2281	1	0.022444	0.020811	0.019042	0.01615	0.014457	0.008586	
4332	2308	1	0.012886	0.012812	0.01172	0.01015	0.01269	0.013443	
4305	2325	1	0.01882	0.01606	0.014699	0.01205	0.012771	0.011448	
4260	2347	1	0.029322	0.02716	0.025323	0.023018	0.02546	0.022231	
4210	2375	1	0.045577	0.043284	0.040124	0.036554	0.040515	0.027363	
4170	2398	1	0.061405	0.060439	0.058425	0.0567026	0.056132	0.056986	
4135	2416	1	0.055294	0.054485	0.051794	0.048184	0.051244	0.046344	
4105	2436	1	0.061598	0.061575	0.060438	0.056333	0.062871	0.066080	
4050	2463	1	0.11037	0.1132	0.1131	0.11289	0.10222	0.1122	
4040	2475	1	0.091498	0.094281	0.091661	0.091751	0.096914	0.090604	
total		0	88	88	88.3	86.2	87.2	89.2	87.4

TABLE 9.2

"Sample" MC1 obtained by densification					
		MC1	9B	9D	9G
Fraction in Mixture			0,889	-0,276	0,387
λ (cm ⁻¹)	λ (nm)				
4720	2119	0,001175932	0,0012043	0,00076051	0,00081253
4670	2141	0,017365599	0,018971	0,014737	0,011765
4640	2155	0,017767782	0,019076	0,014281	0,012239
4615	2167	0,024118931	0,025324	0,019435	0,01796
4585	2181	0,019041012	0,020612	0,016021	0,013237
4485	2230	0,011987639	0,011885	0,010242	0,010952
4460	2242	0,017122848	0,017086	0,015362	0,015912
4385	2281	0,091829933	0,089813	0,09165	0,096098
4332	2308	0,1300549	0,12812	0,12815	0,13281
4305	2323	0,11911918	0,11606	0,1205	0,12682
4260	2347	0,09859607	0,09716	0,099018	0,10194
4210	2375	0,064520009	0,063284	0,066654	0,068709
4170	2398	0,061986802	0,060439	0,067026	0,068963
4135	2418	0,060186195	0,058485	0,065184	0,06749
4105	2436	0,062468569	0,061975	0,066333	0,066187
4060	2463	0,110237982	0,11622	0,11289	0,098096
4040	2475	0,093415832	0,094281	0,091751	0,090004
MON00		88,4	88,3	87,2	87,6

TABLE 9.3

"Sample" MC1 obtained by densification					
		MC2	9B	9C	9D
Fraction in Mixture			1,162	0,24	-0,402
λ (cm-1)	λ (nm)				
4720	2119	0,001178718	0,0012043	0,00035436	0,00076051
4670	2141	0,017275892	0,018971	0,0048161	0,014737
4640	2155	0,01792139	0,019076	0,0062335	0,014281
4615	2167	0,023747506	0,025324	0,0088912	0,019435
4585	2181	0,019544078	0,020612	0,0084724	0,016021
4485	2230	0,011946806	0,011885	0,0093905	0,010242
4460	2242	0,017153608	0,017086	0,01448	0,015362
4385	2281	0,091428926	0,089813	0,099623	0,09165
4332	2308	0,13153274	0,12812	0,14239	0,12815
4305	2323	0,11829752	0,11606	0,13282	0,1205
4260	2347	0,098798684	0,09716	0,1071	0,099018
4210	2375	0,06434942	0,063284	0,073368	0,066654
4170	2398	0,061427506	0,060439	0,075591	0,067026
4135	2418	0,059908962	0,058485	0,075639	0,065184
4105	2436	0,062810524	0,061975	0,072756	0,066333
4060	2463	0,11139522	0,11622	0,090539	0,11289
4040	2475	0,09128022	0,094281	0,07754	0,091751
MON00		88,2	88,3	86	87,2

TABLE 9.4

Determination of MON of reformate based on "Samples" generated						
		Weight	Reformate 9A		MC1	MC2
			Measured	Estimated		
Proximity Index				0,000009271	0,000010043	0,000013457
λ (nm-1)	λ (nm)					
4720	2119	1	0,0010981	0,0011773	0,0011759	0,0011787
4670	2141	1	0,017744	0,017321	0,017366	0,017276
4640	2155	1	0,018144	0,017845	0,017768	0,017922
4615	2167	1	0,024297	0,0239335	0,024119	0,023748
4585	2181	1	0,020515	0,0192925	0,019041	0,019544
4485	2230	1	0,012619	0,011968	0,011988	0,011948
4460	2242	1	0,018197	0,0171385	0,017123	0,017154
4385	2281	1	0,092064	0,0916295	0,09183	0,091429
4332	2308	1	0,12886	0,130795	0,13006	0,13153
4305	2323	1	0,11882	0,11871	0,11912	0,1183
4260	2347	1	0,098322	0,098697	0,098596	0,098798
4210	2375	1	0,064577	0,064435	0,06452	0,06435
4170	2398	1	0,061405	0,0617075	0,061987	0,061428
4135	2418	1	0,059296	0,0600475	0,060186	0,059909
4105	2436	1	0,06198	0,06264	0,062469	0,062811
4060	2463	1	0,11037	0,110815	0,11024	0,11139
4040	2475	1	0,091698	0,092348	0,093416	0,09128
MON00		0	88	88,3	88,4	88,2

TABLE 9.5

Recognition of new sample by auto adjustment					
		Weight	Measured	Estimated	9A
Proximity Index				0,000012235	0,000012235
λ (cm ⁻¹)	λ (nm)				
4720	2119	1	0,0010702	0,0010981	0,0010981
4670	2141	1	0,0171	0,017744	0,017744
4640	2155	1	0,017768	0,018144	0,018144
4615	2167	1	0,024103	0,024297	0,024297
4585	2181	1	0,020269	0,020515	0,020515
4485	2230	1	0,012224	0,012619	0,012619
4460	2242	1	0,018338	0,018197	0,018197
4385	2281	1	0,091998	0,092064	0,092064
4332	2308	1	0,1306	0,12886	0,12886
4305	2323	1	0,11841	0,11882	0,11882
4260	2347	1	0,098802	0,098322	0,098322
4210	2375	1	0,06262	0,064577	0,064577
4170	2398	1	0,060234	0,061405	0,061405
4135	2418	1	0,059762	0,059296	0,059296
4105	2436	1	0,062527	0,06198	0,06198
4060	2463	1	0,11151	0,11037	0,11037
4040	2475	1	0,092677	0,091698	0,091698
MON00			87,9	88	88

Claims

1. A method of determining or predicting a value P_x of a property of a material X or a property of a product of a process from said material or yield of said process, which method comprises measuring the absorption D_x of said material at more than one wavelength in the region 600-2600 nm, comparing the said absorptions or a derivative thereof with absorptions D_m or derivatives thereof at the same wavelength for a number of standards S in a bank for which the said property or yield P is known, and choosing from the bank at least one standard S_m with property P_m said standard having the smallest average value of the absolute difference at each wavelength i between the absorption D_x (or derivative thereof) for the material and the absorption D_m (or derivative thereof) for the standard S_m to obtain P_x , with averaging of said properties or yields P_m when more than one standard S_m is chosen.
2. A method according to claim 1 wherein the standard S_m chosen for the property or yield wanted is such that in relation to the unknown material X and each chosen standard S_m the following functions is met

$$\frac{\sum_{i=1}^n |D_x - D_m|}{n} < \text{experimental error}$$

wherein i_{xm} is the proximity index and is defined by $i^2(xm) = \Sigma(D_{ik} - D_{im})^2$ and the experimental error is in determining said property or yield in the standard.

3. A method according to claim 2 wherein the proximity index is less than the minimal index i_m which has been determined from the standards Sa, Sb, Sc by (a) calculating for each pair of standards Sa/Sb, Sa/Sc the value of $i^2(a,b)$ etc, (b) relating the values of $i^2(a,b)$ etc to the corresponding differences EP (ab) in properties Pa, Pb etc (c) calculating for each value L for which $i^2(ab)$ is $\leq L$, the average of the corresponding differences EPab, (d) calculating Minimal Index from the value of minimal index $i^2(ab)$ where average EPab is the same as reproducibility standard for the property.

4. A method according to any one of the preceding claims, wherein the properties of synthetic standards, which are mixtures, and their spectra for consideration for possible choice for S_m are estimated from existing standards in the bank for which, in respect of each existing standard for use in said mixture equation (4) and (5) are met,

$$\text{Min}C_j - u_j \leq C_{j0} \leq \text{Max} C_j + u_j \quad (4)$$

$$\text{and } \Sigma C_j = 1 \quad (5)$$

wherein C_j is fraction of component j in the sample i

Min C_j is the minimum of j in the samples for which the method is to be used

Max C_j is the maximum of j in the samples for which the method is to be used
 u_j is between 1.0 and 0.05.

5. A method according to any one of claims 2-4 wherein properties of Standards and spectra for consideration for possible choice are estimated by interpolation from measured properties of Standards and spectra for which the proximity index with respect to the unknown X is not more than 10 times the Minimal Index.
6. A method according to claim 4 or 5 wherein at least one of (i) the estimated Standards and the corresponding spectra, and (ii) the property P_x of the unknown material and its spectrum, are added to the bank.
7. A method according to any one of the preceding claims wherein the property is a physicochemical property of material X .
8. A method according to any one of claims 1-6 wherein the property is a physicochemical property or yield of a product of a process to which at least one material X is a feed.
9. A method for adding an extra synthetic standard to a bank of known standards, each of which relates at least one absorption in the 600-2500nm region (or derivative thereof) of a known material to a known property related to that material, which property is of said material which is a feed to a process, or is of a product from said process or yield of said process, which method comprises choosing from the bank at least 2 standards for which equations 4 and 5 (as defined in claim 4) are met, considering mixing the chosen standards in at least one proportion to produce at least one mixture for use in a synthetic standard, and estimating the spectrum of said mixture according to equation 6

$$S_{Mi} = \Sigma C_{ij} X S_j \quad (6)$$

where S_j is the spectrum in the mixture of component j in the calibration matrix,
 and estimating a property of said mixture according to equation 7

$$P_{Mi} = \Sigma C_{ij} X P_j \quad (7)$$

where P_j is the property of component j ,

and then adding the spectrum and property of each "mixture" to the bank, and using them in at least one model involving a correlation/regression approach to relate NIR spectra to at least one property.

10. A method according to any one of claims 1-9 wherein said process is a hydrocarbon conversion or separation process, preferably a reforming or catalytic cracking or hydrotreatment, or distillation or blending.
11. A method according to claim 10 wherein said process is a distillation to give at least 1 distillation product and a residue and the properties/yields are obtained in respect of said product and/or residue.

12. A method according to any one of claims 1-11, wherein said property is in respect of a motor fuel and is at least one of an Octane Number, vapour pressure, volatility, percentage distilled at 70 and at 100°C, gum content in mg/100ml and content of sulphur, benzene, oxygen, methanol, ethanol, ter-butyl alcohol, methyl tert. butyl ether, TAME.
13. A method according to claim 12 wherein the property is in respect of a blend comprising gasoline the spectra are measured on feeds to said blending, and by calculation the blend index obtained as a linear or non linear function.
14. A method according to any one of claims 1-11 wherein said property is in respect of gas oil and is at least one of cetane index, cetane number, percentage of sulphur, density at 15°C, flash point, cloud point, filterability and viscosity at 40°C.
15. A method according to any one of claims 1-10 wherein said property is in respect of a crude oil and is at least one of density, percentage of sulphur, viscosity at 100°C, content of paraffin, distillation curve and residual carbon percentage (Conradson Carbon).
16. A method according to any one of claims 1-10 wherein said property is in respect of a feed to a reforming process and is at least one of percentages of saturated linear, isoparaffins, napthenics, and aromatics and density.
17. A method according to any one of claims 1-10 wherein said property is in respect of a feed to a fluid catalytic cracking unit and is at least one of the density, the weight percentage of sulphur, the aniline point, viscosity at 100°C, refractive index at 20°C or 60°C, 50% distillation point, molecular weight, percentage of aromatic carbon and the KUOP, crackability or cokability of the feed or yield of gas, gasoline, gas oil or residue.
18. A method according to any one of claims 1-10 wherein said percentage is in respect of the feed to a hydrogenation unit and is at least one of percentages of linear paraffins, isoparaffins, napthenes, linear olefins, cyclic olefins, dienes, benzene, toluene, xylene, alkylbenzene, density, or yield of light cut, heavy cut, or raffinate or benzene.
19. Apparatus suitable for use in the method of any one of the preceding claims which comprises an NIR spectrometer receiving at least one signal from a feed or product line in said process and being coupled to a computer to effect continuous measurement of the spectra of the feed and/or product and provide feed back control of the process.



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Application Number
EP 94 43 0009

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO-A-92 07326 (EXXON RESEARCH) 30 April 1992 PAGES 9-12;24-28:32-34 ---	1, 19 G01N21/35 G01N33/28
A	JOURNAL OF CHEMOMETRICS, vol.1, no.1, 1 October 1987 pages 121 - 134 NAES ET AL. 'THE DESIGN OF CALIBRATION IN NEAR INFRA-RED, ETC.' * page 122 - page 126 * ---	1
A	APPLIED SPECTROSCOPY, vol.44, no.7, 1 July 1990 pages 1152 - 1158 ISAKSSON ET AL. 'SELECTION OF SAMPLES FOR CALIBRATION, ETC.' ---	1
A	ANALYTICAL CHEMISTRY, vol.55, no.11, 1 September 1983 pages 1694 - 1703 MARIS ET AL. 'NONLINEAR MULTICOMPONENT ANALYSIS, ETC.' ---	1, 9
A	APPLIED SPECTROSCOPY, vol.41, no.7, 1 July 1987 pages 1204 - 1213 WHITFIELD ET AL. 'NEAR INFRARED SPECTRUM QUALIFICATION, ETC.' ---	1 G01N G01D
A, D	EP-A-0 305 090 (BP OIL INT.) 1 March 1989 PAGES 4-6;EXAMPLES ---	1, 9-19
A	ANALYTICAL CHEMISTRY, vol.60, no.6, 15 March 1988 pages 569 - 573 PUCHWEIN 'SELECTION OF CALIBRATION SAMPLES, ETC.' --- -/-	1
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
THE HAGUE	4 April 1995	Boehm, C
CATEGORY OF CITED DOCUMENTS		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		F : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : number of the same patent family, corresponding document

EP 0 706 040 A1 (PCT/CA)



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Application Number
EP 94 43 0009

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	ANALYTICAL CHEMISTRY, vol.57, no.12, 1 October 1985 pages 2299 - 2303 HONIGS ET AL. 'UNIQUE SAMPLE SELECTION, ETC.' -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 4 April 1995	Examiner Boehm, C
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